

TITLE OF THE INVENTION

**METHOD AND SYSTEM FOR PERFORMING ATOMIC LAYER DEPOSITION**

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application is related to pending United States patent application serial no. 10/487,232, filed on February 26, 2004, the entire contents of which are herein incorporated by reference.

BACKGROUND OF THE INVENTION

Field of Invention

[0002] The present invention relates to plasma processing and more particularly to a method for improved plasma processing.

Description of Related Art

[0003] Typically, during materials processing, plasma is employed to facilitate the addition and removal of material films when fabricating composite material structures. For example, in semiconductor processing, a (dry) plasma etch process is utilized to remove or etch material along fine lines or within vias or contacts patterned on a silicon substrate. Alternatively, for example, a vapor deposition process is utilized to deposit material along fine lines or within vias or contacts on a silicon substrate. In the latter, vapor deposition processes include chemical vapor deposition (CVD), and plasma enhanced chemical vapor deposition (PECVD).

[0004] In PECVD, plasma is utilized to alter or enhance the film deposition mechanism. For instance, plasma excitation generally allows film-forming reactions to proceed at temperatures that are significantly lower than those typically required to produce a similar film by thermally excited CVD. In addition, plasma excitation may activate film-forming chemical reactions that are not energetically or kinetically favored in thermal CVD. The chemical and

physical properties of PECVD films may thus be varied over a relatively wide range by adjusting process parameters.

- [0005] More recently, atomic layer deposition (ALD), a form of PECVD or more generally CVD, has emerged as a candidate for ultra-thin gate film formation in front end-of-line (FEOL) operations, as well as ultra-thin barrier layer and seed layer formation for metallization in back end-of-line (BEOL) operations. In ALD, two or more process gasses are introduced alternately and sequentially in order to form a material film one monolayer at a time.
- [0006] As the feature size shrinks and the number and complexity of the deposition process steps used during integrated circuit (IC) fabrication escalate, the ability to control the transport of deposition materials within such features becomes more stringent.
- [0007] Moreover, as feature sizes progressively shrink, they do so at a rate greater than a rate at which the film thicknesses shrink. Therefore, the feature aspect ratio (feature depth-to-width) is greatly increased with shrinking sizes (of order 10:1). As the aspect ratio increases, the specie transport local to the features becomes increasingly important in order to preserve the conformality of the deposition within the feature.

#### SUMMARY OF THE INVENTION

- [0008] One object of the present invention is to reduce or eliminate any or all of the above-described problems.
- [0009] Another object of the present invention is to provide a method of depositing a material with improved deposition characteristics.
- [0010] Yet another object of the invention is to provide a method for improving the conformality of a deposition layer within high aspect ratio features.
- [0011] These and/or other objects of the present invention are provided by a method and system for performing atomic layer deposition. According to one aspect of the invention an atomic layer deposition system includes a process chamber; a substrate holder provided within the process chamber and configured to support a substrate; and a gas injection system configured to supply a first precursor and a second precursor to the process chamber. A

controller is configured to control the gas injection system to continuously flow the first precursor to the process chamber and to pulse the second precursor to the process chamber at a first time, the controller being configured to pulse a RF power to the substrate holder at a second time in order to sequentially deposit at least one monolayer on the substrate.

[0012] According to another aspect of the invention, a method of operating a plasma processing system in order to deposit a film on substrate using atomic layer deposition (ALD) includes the steps of: adjusting a background pressure in a process chamber, wherein the background pressure is established by flowing a first gas flow of a first precursor using a gas injection system; igniting a processing plasma in the process chamber; pulsing a second gas flow of a second precursor using the gas injection system at a first time; pulsing a RF power to a substrate holder at a second time; and sequentially depositing at least one monolayer of the film using the first precursor and the second precursor.

#### BRIEF DESCRIPTION OF THE DRAWINGS

- [0013] In the accompanying drawings:
- [0014] FIG. 1 depicts a schematic view of a plasma processing device according to an embodiment of the present invention;
- [0015] FIG. 2 is a timing diagram for gas injection pulsing and RF bias pulsing according to the embodiment of FIG. 1; and
- [0016] FIG. 3 outlines a procedure for operating the system of FIG. 1 according to the embodiment of FIG. 1.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

- [0017] In order to improve deposition characteristics particularly in high aspect ratio features, the present invention improves a plasma processing system and method of operation to affect improvements in chemical transport local to an exposed substrate surface. The exposed substrate surface is exposed to material deposition steps, the combination of which serve to alter the material composition and/or topography of the exposed substrate surface. For

example, deposition systems can include physical vapor deposition (PVD) systems, plasma-enhanced chemical vapor deposition (PECVD) systems, and atomic layer deposition (ALD) systems. For instance, in ALD processes, one or more gases can be pulsed with the flow of a continuous gas to form thin films of metal, metal nitride, metal oxide, nitrides, and oxides one monolayer at a time. One aspect of material deposition is chemical transport, which can be severely limited in high aspect ratio features due to the low densities associated with low pressure processing and lack of chemical transport directivity local to substrate material features. Without adequate chemical transport, monolayer deposition may not conform to the contour of the high aspect ratio feature as desired. A method is described herein of periodically pulsing a gas flow in conjunction with pulsing the RF power to the substrate holder in order to affect improvements to chemical transport proximate the substrate.

[0018] Pulsing the gas flow leads to an increase of the gas pressure proximate an exposed surface of a substrate, hence, causing a local reduction in the mean free path, i.e. an increase in the probability for collisions local to the substrate surface. Pulsing the RF power to the substrate holder leads to an increase in the potential drop across the sheath for a duration characteristic of the pulse width during which the sheath thickness is enlarged. The subsequent reduction of the mean free path to values less than the sheath thickness leads to a significantly greater probability during this short period of time for ion-neutral collisions, either charge exchange collisions or simply momentum transfer collisions, which, in turn, create a greater population of energetic, directional neutral species moving in a direction of normal incidence to the substrate surface. Therefore, the normal flux of mass and momentum is increased at a feature entrance. This results in improved chemical transport at the substrate surface which facilitates atomic layer deposition, and in particular can improve conformality of deposition within high aspect ratio features. The plasma processing system and its method of operation according to the present invention is now described.

[0019] The present invention generally relates to a plasma processing system including a gas injection system capable of continuously providing a first process gas through a first array of gas injection orifices and pulsing a second process gas through a second array of gas injection orifices. The processing system further includes a RF bias applied to a substrate holder upon which a substrate rests. The substrate is exposed to a plasma process to facilitate an addition (deposition) or a removal (etching) of a material to or from the substrate.

[0020] A plasma processing system 1 is shown in FIG. 1 including a plasma processing chamber 10 wherein a gas injection plate 12 of gas injection system 11 is positioned directly opposite a substrate holder 14 to which a substrate 16 is attached. The gas injection system 11 facilitates a continuous injection of a first gas flow 20 and a pulsed injection of a second gas flow 30 into plasma processing chamber 10 through gas injection plate 12. The continuous flow of the first gas flow 20 originates from a first gas supply 26 through a mass flow controller 24 via a gas line 22. The pulsed flow of the second gas flow 30 originates from a second gas supply 36 through a pulsed gas injection manifold 34 via a gas line 32.

[0021] The processing system 1 of FIG. 1 further includes a RF bias originating from oscillator 50 and applied to substrate holder 14 through impedance match network 52. An amplifier 54 increases the amplitude of RF bias signal output from oscillator 50 subject to amplitude modulation via signal 58 output from waveform signal generator 56. The amplifier 54 sends the amplified RF bias signal to the impedance match network 52.

[0022] With continuing reference to FIG. 1, substrate holder 14 is biased with RF power, wherein an RF signal originating from oscillator 50 is coupled to substrate holder 14 through impedance match network 52 and amplifier 54. Signal amplification is subjected to amplitude modulation via input signal 58 from a waveform signal generator 56.

[0023] The amplifier 54 can be a linear RF amplifier suitable for receiving an oscillator input from oscillator 50 and an amplitude modulation signal 58 from waveform signal generator 56. One example of a signal 58 output from

waveform signal generator 56 is a pulse waveform. An exemplary system including the amplifier 54 and an internal pulse generator is a commercially available linear RF amplifier (Model line LPPA) from Dressler (2501 North Rose Drive, Placentia, CA 92670). The above amplifier is capable of operating in continuous mode as well as pulse mode with RF powers ranging from 400 to 8000W at frequencies ranging from 10 to 500 MHz. Moreover, the above amplifier can achieve pulse widths as short as 20 milliseconds.

[0024] Impedance match network 52 serves to maximize the transfer of RF power to plasma in processing chamber 10 by minimizing the reflected power. Match network topologies (e.g. L-type,  $\pi$ -type, T-type, etc.) for achieving this end are known. Match network settings for tuning capacitors C1 and C2 in, for example, an L-type configuration, are controlled via controller 70 during both start and run-time conditions. Preferably, an automatic match network control methodology is employed to maintain optimal match throughout the entirety of the process. However, the response for typical match networks is approximately 150 milliseconds. Therefore, it is not expected that a conventional (mechanically tuned) match network can respond optimally to pulse widths less than approximately 150 milliseconds. In such a case, a conventional match network is designed for run and start set-points based upon the continuous flow process gas conditions. If on the other hand, pulse widths in excess of several hundred milliseconds are employed, conventional match networks are sufficiently fast to respond and provide an optimal impedance match even during pulsing periods. Further discussion is provided below.

[0025] Additionally, the processing system 1 of FIG. 1 further includes a vacuum pump system 42 through which process gases and effluent gases can be removed (or evacuated) from plasma processing chamber 10. Vacuum pump system 42 preferably includes a turbo-molecular vacuum pump (TMP) capable of a pumping speed up to 5000 liters per second (and greater) and a gate valve for throttling the chamber pressure. TMPs are useful for low pressure processing, typically less than 50 mTorr. At higher pressures, the TMP pumping speed falls off dramatically. For high pressure processing (i.e.

greater than 100 mTorr), a mechanical booster pump and dry roughing pump is recommended.

- [0026] Furthermore, the plasma processing system 1 further includes a controller 70 coupled to vacuum pump system 42, impedance match network 52, amplifier 54 and waveform signal generator 56. In addition, controller 70 is coupled to mass flow controller 24, first gas supply 26, second gas supply 36 and pulsed gas injection manifold 34 for the purpose of controlling gas injection parameters in the plasma processing system 1.
- [0027] Controller 70 includes a microprocessor, memory, and a digital I/O port capable of generating control voltages sufficient to communicate and activate inputs to the gas injection system 11. Moreover, controller 70 exchanges information with impedance match network 52, amplifier 54, and waveform signal generator 56. The controller 70 exchanges status data with the gas supplies 26 and 36, mass flow controller 24, and pulsed gas injection manifold 34. In addition, controller 70 sends and receives control signals to and from vacuum pump 55. For example, a gate valve can be controlled. A program stored in the memory includes a process recipe with which to activate the valves and the respective gas flow rate when desired. One example of controller 70 is a Model # SBC2486DX PC/104 Embeddable Computer Board commercially available from Micro/sys, Inc., 3730 Park Place, Glendale, CA 91020.
- [0028] During the operation of the plasma processing system 1, process gas is introduced to the plasma processing chamber 10 via gas injection system 11 which continuously flows the first gas flow 20 and pulses the second gas flow 30. First and second gas flows 20 and 30 originate from gas supplies 26 and 36, respectively. Gas supplies 26 and 36 can include a cabinet housing a plurality of compressed gas cylinders and can include pressure regulators for safe gas handling practice. The continuous flow of first gas flow 20 may be achieved via a gas showerhead configuration that is well known to those skilled in the art.
- [0029] In a preferred embodiment, continuous flow of first gas flow 20 is introduced to the process chamber 10 through gas injection plate 12. In an alternate

embodiment, continuous flow of gas flow 20 is introduced to the process chamber 10 through a chamber wall of the process chamber 10. In a preferred embodiment, mass flow controller 24 monitors and controls the mass flow rate of the first process gas being supplied by gas supply 26. The pulsing of second gas 30 is achieved via pulsed gas injection manifold 34. The pulsed gas injection manifold 34 can include one or more pressure regulators, one or more pulsed gas injection valves and a gas distribution manifold. An exemplary pulsed gas injection system is described in greater detail in pending U.S. application 60/272,452, filed on March 2, 2001, which is incorporated herein by reference in its entirety. In a preferred embodiment, pulsed flow of second gas flow 30 is introduced to process chamber 10 through gas injection plate 12.

- [0030] In alternate embodiments, gas injection plate 12 can be machined from a metal such as aluminum and, for those surfaces in contact with the plasma, can be anodized to form an aluminum oxide protective coating or spray coated with  $Y_2O_3$ . Furthermore, the gas inject plate 12 can be fabricated from silicon or carbon to act as a scavenging plate, or it can be fabricated from silicon carbide to promote greater erosion resistance.
- [0031] Substrate 16 is transferred into and out of plasma processing chamber 10 by means well understood to those skilled in the art. Furthermore, substrate 16 is preferably affixed to the substrate holder 14 via an electrostatic clamp (not shown), and backside gas (not shown) can be provided for improved thermal conductance between substrate 16 and substrate holder 14. Substrate holder 14 can further include heating and cooling mechanisms (not shown) in order to facilitate temperature control of substrate 16.
- [0032] FIG. 2 presents a schematic illustration of a method of operating the embodiment described in FIG. 1. A first time history of a flow rate of the first gas flow 20, generally indicated as 110, is shown, wherein the flow rate 112 is maintained constant during the length of the process. A second time history of a flow property of the second gas flow 30, generally indicated as 120, is shown, wherein the flow property 122 is preferably an injection total pressure. The injection total pressure is pulse modulated via pulsed gas injection

manifold 34 with a pulse amplitude 122, pulse width 126 and pulse period 124. A ratio of the pulse width 126 to the pulse period 124 can further be referred to as the pulse duty cycle. In addition, the pulsed flow property 122 can be a mass flow rate of the second gas flow 30.

[0033] In concert with the first and second time histories, a third time history of the RF bias power, generally indicated as 130, is shown, wherein the RF bias power is pulse modulated between a first power level 134 and a second power level 132. The RF bias power pulse has a pulse width 138 and a pulse period 136. A ratio of the pulse width 138 to the pulse period 136 can be further referred to as the pulse duty cycle. In a preferred embodiment, the RF power pulse width 138 and pulse period 136 are substantially equivalent to the second process gas pulse width 122 and pulse period 124, respectively. In an alternate embodiment, the RF power pulse duty cycle is substantially equivalent to the second gas flow pulse duty cycle. In an alternate embodiment, the second gas flow pulse width is substantially different than the RF power pulse width. In an alternate embodiment, the second gas flow pulse period is substantially different than the RF power pulse period. In an alternate embodiment, the second gas flow duty cycle is substantially different than the RF power pulse duty cycle. In a further alternate embodiment, the RF power pulse waveform is shifted or offset in time 140 relative to the second gas flow gas pulse waveform.

[0034] The flow rate of the first gas flow 20 can range from 100 to 5000 sccm (equivalent argon flow rate). A chamber pressure can range from 1 to 1000 mTorr. The injection total pressure of the second gas flow 30 gas can range from 50 to 1000 Torr. The pulse widths can range from 1 to 1000 milliseconds with pulse periods ranging from 10 milliseconds to 10 seconds.

[0035] In one embodiment, an atomic layer deposition (ALD) process according to the method of operation presented in FIG. 2 is now described. The first gas flow 20 can include a first precursor with or without a carrier gas. Additionally, the second gas flow 30 can include a second precursor with or without a carrier gas. For example, the carrier gas can include an inert gas, such as a

Noble gas (i.e., He, Ne, Ar, Kr, Xe, Rn). The first precursor and the second precursor can be selected depending upon the material to be deposited.

- [0036] In one example, when depositing tungsten, the first precursor can include WF<sub>6</sub>, or W(CO)<sub>6</sub>, and the second precursor can include H<sub>2</sub>.
- [0037] In another example, when depositing tungsten nitride, the first precursor can include WF<sub>6</sub>, and the second precursor can include NH<sub>3</sub>, or N<sub>2</sub> and H<sub>2</sub>.
- [0038] In another example, when depositing tantalum, the first precursor can include TaCl<sub>5</sub>, and the second precursor can include H<sub>2</sub>.
- [0039] In another example, when depositing tantalum pentoxide, the first precursor can include TaCl<sub>5</sub>, and the second precursor can include H<sub>2</sub>O, or H<sub>2</sub> and O<sub>2</sub>.
- [0040] In another example, when depositing tantalum nitride (i.e., TaN<sub>x</sub>), the first precursor can include a tantalum containing precursor, such as TaCl<sub>5</sub>, PDEAT (pentakis(diethylamido) tantalum), PEMAT (pentakis(ethylmethylamido) tantalum), TaBr<sub>5</sub>, or TBTDET (t-butylimino tris(diethylamino) tantalum). The second precursor can include a mixture of H<sub>2</sub> and N<sub>2</sub>.
- [0041] In another example, when depositing molybdenum, the first precursor can include molybdenum hexafluoride, and the second precursor can include H<sub>2</sub>.
- [0042] In another example, when depositing copper, the first precursor can include organometallic compounds, such as Cu(TMVS)(hfac), or (Trimethylvinylsilyl) hexafluoroacetylacetone Copper I, also known by the trade name CupraSelect®, available from Schumacher, a unit of Air Products and Chemicals, Inc., 1969 Palomar Oaks Way, Carlsbad, Calif. 92009), or inorganic compounds, such as CuCl. The second precursor can include at least one of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, or H<sub>2</sub>O. As used herein, the term “at least one of A, B, C, ... or X” refers to any one of the listed elements or any combination of more than one of the listed elements.
- [0043] In another example, when depositing ZrO<sub>2</sub>, the first precursor can include Zr(NO<sub>3</sub>)<sub>4</sub>, or ZrCl<sub>4</sub>, and the second precursor can include H<sub>2</sub>O.
- [0044] In another example, when depositing HfO<sub>2</sub>, the first precursor can include Hf(NO<sub>3</sub>)<sub>4</sub>, or HfCl<sub>4</sub>, and the second precursor can include H<sub>2</sub>O.
- [0045] In another example, when depositing Hf, the first precursor can include HfCl<sub>4</sub>, and the second precursor can include H<sub>2</sub>.

- [0046] In another example, when depositing niobium, the first precursor can include niobium pentachloride, and the second precursor can include H<sub>2</sub>.
- [0047] In another example, when depositing zinc, the first precursor can include zinc dichloride, and the second precursor can include H<sub>2</sub>.
- [0048] In another example, when depositing SiO<sub>2</sub>, the first precursor can include Si(NO<sub>3</sub>)<sub>4</sub>, and the second precursor can include H<sub>2</sub>O.
- [0049] In another example, when depositing SiO<sub>2</sub>, the first precursor can include dichlorosilane, and the second precursor can include H<sub>2</sub>.
- [0050] In another example, when depositing SiO<sub>2</sub>, the first precursor can include SiCl<sub>4</sub>, and the second precursor can include H<sub>2</sub>O, or H<sub>2</sub> and O<sub>2</sub>.
- [0051] In another example, when depositing silicon nitride, the first precursor can include SiCl<sub>4</sub>, or dichlorosilane, and the second precursor can include NH<sub>3</sub>, or N<sub>2</sub> and H<sub>2</sub>.
- [0052] In another example, when depositing TiN, the first precursor can include Ti(NO<sub>3</sub>), and the second precursor can include NH<sub>3</sub>.
- [0053] In another example, when depositing Ti, the first precursor can include titanium tetrachloride, or titanium tetraiodide, and the second precursor can include H<sub>2</sub>.
- [0054] In another example, when depositing titanium oxide, the first precursor can include titanium tetrachloride, or titanium tetraiodide, and the second precursor can include H<sub>2</sub>O, or H<sub>2</sub> and O<sub>2</sub>.
- [0055] In another example, when depositing TiN, the first precursor can include titanium tetrachloride, and the second precursor can include NH<sub>3</sub>.
- [0056] In another example, when depositing Ti, the first precursor can include tetrakis(diethylamino)titanium or tetrakis(dimethylamino)titanium, and the second precursor can include H<sub>2</sub>.
- [0057] In another example, when depositing TiN, the first precursor can include tetrakis(diethylamino)titanium or tetrakis(dimethylamino)titanium, and the second precursor can include NH<sub>3</sub>.
- [0058] In another example, when depositing aluminum, the first precursor can include aluminum trichloride, or trimethylaluminum, and the second precursor can include H<sub>2</sub>.

- [0059] In another example, when depositing aluminum nitride, the first precursor can include aluminum trichloride, or trimethylaluminum, and the second precursor can include NH<sub>3</sub>, or N<sub>2</sub> and H<sub>2</sub>.
- [0060] In another example, when depositing aluminum oxide, the first precursor can include aluminum trichloride, or trimethylaluminum, and the second precursor can include H<sub>2</sub>O, or O<sub>2</sub> and H<sub>2</sub>.
- [0061] In another example, when depositing GaN, the first precursor can include gallium nitrate, or trimethylgallium, and the second precursor can include NH<sub>3</sub>.
- [0062] In another example, when depositing Cr, the first precursor can include Cr oxo-nitrate, and the second precursor can include H<sub>2</sub>.
- [0063] The second precursor can, for example, be at least one of H<sub>2</sub>, O<sub>2</sub>, N<sub>2</sub>, NH<sub>3</sub>, H<sub>2</sub>O, or H<sub>2</sub>O<sub>2</sub>.
- [0064] According to this embodiment, a chamber pressure can be set for the continuous flow of the first precursor, with or without a carrier gas. The background pressure can, for example, range from 5 to 200 mTorr, for example, by sensing the chamber pressure in the pumping port or at the chamber wall outside of the processing region and adjusting the vacuum pump system gate valve. The second gas flow can include a pulsed injection of the second precursor. The gas injection total pressure for the second gas flow is preferably atmospheric pressure (i.e. approximately 760 Torr). And lastly, pulse widths and pulse periods are substantially equivalent for the second gas flow pulse and the RF power pulse and are set at 5 to 20 milliseconds, and 10 to 40 milliseconds, respectively.
- [0065] In this method of operation, process gas pulse widths of 5 to 20 milliseconds can be achieved via gas injection configurations presented in pending U.S. application 10/469,592, and RF power pulse widths of 5 to 20 milliseconds are achieved via commercially available RF power sources as described above. Also described above, when RF power pulse widths are less than the response time of conventional impedance match networks (i.e. approximately 150 milliseconds), alternative techniques could be required to achieve an optimal impedance match. Linear RF amplifiers, as described above, are now being equipped with frequency shift tuning and, in particular, they are

available for frequencies of 1.6 to 4 MHz (Dressler RF Technology). For frequencies in excess of commercially viable options, alternative solutions may be required such as a free running oscillator as described in pending U.S. application 10/043,270 filed on January 14, 2002, which is incorporated herein by reference in its entirety.

[0066] In FIG. 3, a method of operating the embodiment depicted in FIG. 1 is presented. A plasma process is initiated in plasma processing system 1 at step 500. In step 510, controller 70 initiates a flow rate 112 for the first gas flow 20 through gas injection system 11 according to a stored process recipe. The first gas flow 20 is continuously introduced to process chamber 10 with a substantially constant mass flow rate 112 from the start of the process in step 500 until the end of the process in step 630. In step 520, controller 70, coupled to vacuum pump system 42, adjusts the background pressure in process chamber 10 according to a stored process recipe.

[0067] Once the first process gas flow rate is established and the background pressure is set, a processing plasma is ignited via substrate holder RF power in step 530 according to a process recipe stored in controller 70. In step 540, controller 70 triggers second gas flow pulse in step 550 and RF power pulse in step 580 with or without a phase delay in step 570. The second gas flow pulse is ended in step 560 while the RF power pulse is ended in step 590, and the process pulse is completed in step 600.

[0068] In step 610, a process endpoint is evaluated per endpoint detection methods such as optical emission spectroscopy, impedance match network component monitoring, etc. If an endpoint is reached, the process comes to an end in step 630. If the process is not complete, a time delay comparable to the respective pulse periods for the second process gas pulse and the RF power pulse is enforced in step 620. Thereafter, steps 540 through 630 are repeated.

[0069] Although only certain exemplary embodiments of this invention have been described in detail above, those skilled in the art will readily appreciate that many modifications are possible in the exemplary embodiments without materially departing from the novel teachings and advantages of this

invention. Accordingly, all such modifications are intended to be included within the scope of this invention.